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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY APR 26 1990			3. DISTRIBUTION / AVAILABILITY OF REPORT DISTRIBUTION STATEMENT A Approved for public release Distribution Unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE DD			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 19			7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6a. NAME OF PERFORMING ORGANIZATION The University of Texas at Arlington		6b. OFFICE SYMBOL (If applicable)		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217
6c. ADDRESS (City, State, and ZIP Code) Center for Advanced Polymer Research Department of Chemistry, Box 19065, University of Texas at Arlington, Arlington, TX, 76019		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Defense Advanced Research Projects Agency		8b. OFFICE SYMBOL (If applicable) DARPA		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1320
8c. ADDRESS (City, State, and ZIP Code) 1410 Wilson Boulevard Arlington, Virginia 22209		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) ELECTRONIC AND IONIC TRANSPORT IN PROCESSABLE CONDUCTING POLYMERS				
12. PERSONAL AUTHOR(S) Martin Pomerantz, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick				
13a. TYPE OF REPORT Quarterly-Technical		13b. TIME COVERED FROM 1/1/90 TO 3/31/90		14. DATE OF REPORT (Year, Month, Day) 1990, April, 10
15. PAGE COUNT 5				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES FIELD GROUP SUB-GROUP			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) 2,5-Disubstituted-1,4-bis(2-heterocycle)benzene polymers, Poly(3-alkylthiophenes), Molecular weight, blends, ion binding, Self-doped polypyrroles, Chemically modified electrodes	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A series of 2,5-disubstituted-1,4-bis(2-heterocycle)benzenes have been synthesized and their respective polymers have been prepared chemically and electrochemically. Good electrical conductivity has been observed for the 2,5-dimethoxy derivative where the heterocycle is thiophene when the polymer is NOPF ₆ doped while the 2,5-dimethyl derivative shows much lower conductivity. Correlations of the electronic properties have been made with theoretically calculated polymer band structures and minimum energy conformations. Multiangle laser light scattering molecular weight GPC studies of a number of different samples of poly(3-octylthiophene) has shown a variation from sample to sample, all being fairly high. Fibers melt spun from blends of poly(3-decylthiophene) and low density polyethylene (LDPE) have been shown by electron microscopy to be phase separated and to actually be composites of the poly(3-decylthiophene) in the LDPE matrix. We have shown that films of self-doped poly-(pyrrole propanesulfonate) tenaciously bind useful photophysical molecules. We have also demonstrated how <i>in situ</i> surface photochemistry at chemically modified electrodes offers a powerful route to catalyst generation at the surface. (f11) R				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Milliken			22b. TELEPHONE (Include Area Code) (202) 696-4410	
			22c. OFFICE SYMBOL	

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY/OFFICE OF NAVAL RESEARCH

Grant N00014-90-J-1320

R&T Code a400008df306

Technical Report No. 19

Electronic and Ionic Transport in Processable Conducting Polymers

by

Martin Pomerantz, Grant Administrator

John R. Reynolds

Krishnan Rajeshwar

Dennis S. Marynick

Center for Advanced Polymer Research

Department of Chemistry

Box 19065

The University of Texas at Arlington

Arlington, TX 76019-0065

April 10, 1990

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Description of Progress

We have prepared 16 bis(2-heterocycle)benzenes using thiophene, furan and pyrrole as the heterocycle. These precursor monomers for the preparation of a new family of conjugated processable polymers are substituted at the 2 and 5 positions of the phenylene ring with methyl, hexyl, methoxy, heptoxy and dodecyloxy substituents to yield both symmetric and unsymmetric molecules. Oxidative polymerization has been accomplished using both chemical (FeCl_3) and electrochemical methods. In the case of the 2-thienyl derivatives, the highest conductivity has been observed for the NOPF_6 doped dimethoxy substituted polymer ($2 \Omega^{-1} \text{ cm}^{-1}$). The dimethyl substituted polymers, however, exhibit significantly lower conductivity ($10^{-6} \Omega^{-1} \text{ cm}^{-1}$). Correlations of the electronic properties of the polymers have been made with theoretically modeled minimum energy conformations and extended Hückel determined band structures. A benefit of the symmetrically substituted polymers is that they contain no configurational isomerism in the form of head-head defects. This is a common problem with the poly(3-alkylthiophenes).

Molecular weight studies of poly(3-alkylthiophenes) using GPC in conjunction with our multiangle laser light scattering (MALLS) detector (which gives absolute molecular weights) has shown that weight average molecular weights for the series where alkyl = C_4H_9 , C_6H_{13} , C_8H_{17} , $\text{C}_{10}\text{H}_{21}$ and $\text{C}_{12}\text{H}_{25}$ varied from 204,000-398,000 and the molecular weight at the maximum in concentration varied from 88,000 to 320,000. These single values at the maximum are the *absolute* molecular weights. We have also prepared several different samples of poly(3-octylthiophene) using FeCl_3 , and have shown that there is a variation in the molecular weights from sample to sample. Thus the weight average molecular weights ranged from 113,000 to 307,000 while the molecular weight at the peak maximum ranged from 73,000 to 160,000. Fibers of blends of poly(3-decylthiophene) with low density polyethylene (40:60 and 20:80) have been prepared in our continuing collaboration with Hoechst-Celanese Research Division, Summit, New Jersey. Electron microscopy has shown that these blend fibers are phase separated and are actually composites of poly(3-decylthiophene) in a matrix of polyethylene. EDAX studies have confirmed this.

Following our initial observations of the ion exchange properties of polypyrrole, we have recently completed quantitative studies on the ion binding properties of "self-doped" poly(pyrrole propanesulfonate) thin films. These studies show that these films can tenaciously bind useful photophysical molecules such as $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridyl). Efforts to extend these findings to photoelectrochemical applications related to solar energy storage are underway.

We have also demonstrated how *in situ* surface photochemistry at chemically modified electrodes offers a powerful route to catalyst generation at the surface. One such "molecularly engineered" system comprises the synthesis of Prussian blue from surface-immobilized ferri-ferrocyanide reaction centers at a quarternized polyvinylpyridine-modified glassy carbon surface. Aside from the intrinsic advantages related to the high *local* concentration (several moles/liter) at chemically modified surfaces, these new heterogeneous (essentially two-dimensional) surfaces offer useful insights and comparisons with the chemistry of their homogeneous (3-D) solution counterparts.

Publications

Papers Published

Qiu, Y-J. and Reynolds, J. R. "Poly[3,6-(carbaz-9-yl)propanesulfonate]: A Self-Doped Polymer with Both Cation and Anion Exchange Properties," *J. Electrochem. Soc.* **1990**, *137*, 900-904.

Sharma, S. C., Krishnamoorthy, S., Naidu, S. V., Eom, C. I., Krichene, S., and Reynolds, J. R. "Positron Annihilation and Conductivity Correlations in Poly(pyrrole tosylate) and Poly(pyrrole fluoride)," *Phys. Rev. B.* **1990**, *41*, 5258-5265.

Shaffer, T. D. and Kramer, M. C., "Cyclization versus Polymerization in Phase Transfer Catalyzed Polythioetherification," *Makromol. Chem.* **1990**, *91*, 71-79.

Papers in Press

Nayak, K. and Marynick, D. S. "The Interplay Between the Geometric and Electronic Structures of Polyisothianaphthene and Polyisnaphthothiophene, Polythieno(3,4-b)pyrazine and Polythieno(3,4-b)quinoxaline," *Macromolecules*, in press.

Gieselman, M. G. and Reynolds, J. R. "Poly(*p*-phenyleneterephthalamide propanesulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites," *Macromolecules*, in press.

Wang, F. and Reynolds, J. R. "Soluble and Electroactive Nickel Bis(dithiolene) Polymers Prepared Via Metal Complexation Polymerization," *Macromolecules*, in press.

Reynolds, J. R. and Pomerantz, M. "Processable Electronically Conducting Polymers," in "Electroresponsive Molecular and Polymeric Systems," Skotheim, T. A., Ed.; Marcel Dekker: New York; Vol. 2, in press.

Basak, S., Rajeshwar, K., and Kaneko, M. "Ion Binding of Poly{pyrrole-co[3-(pyrrol-1-yl)-propanesulfonate]} Thin Films," *Anal. Chem.*, in press.

Papers Submitted for Publication

Reynolds, J. R., Ruiz, J. P., Child, A. D., Marynick, D. S., and Nayak, K. "Electrically Conducting Polymers Containing Alternating Substituted Phenyls and Bithiophene Repeat Units," *Macromolecules*, submitted for publication.

Basak, S., Rajeshwar, K., and Kaneko, M. "In Situ Photogeneration of a Catalyst on a Chemically Modified Electrode Surface: Application to a Mixed Valent Hexacyanoferrate System," *J. Chem. Soc., Chem. Commun.*, submitted for publication.

Shaffer, T. D. and Sheth, K. A. "Mesomorphic Polyazomethine Ethers Containing Dibenzo-18-crown-6 Units," *Makromol. Chem., Rapid Commun.*, submitted for publication.

Meetings Attended and Talks Presented

John Reynolds attended the Gordon Research Conference on Polymer Chemistry, Ventura, California, January, 1990, and presented a paper entitled "Metal Complex Polymers."

John Reynolds attended the 17th Annual Water-Borne and Higher-Solids Coatings Symposium on Advances in Polymer Synthesis, New Orleans, Louisiana, February, 1990, and presented a paper entitled "Electropolymerization in the Synthesis of Conducting Materials."

Krishnan Rajeshwar presented an invited seminar entitled "Charge Transport/Storage in Biconductive Oxides and Polymers" to the Chemistry Department at Texas A&M University, College Station, Texas, March, 1990.

Visitors to UTA

Professor Allan S. Hoffman of the University of Washington presented a seminar at U. T. Arlington on March 26, 1990, entitled "Biomedical Applications of Plasma Polymerization: Two Case Studies: The Small Diameter Vascular Graft and Non-Fouling Surfaces," detailing his program in the surface properties of polymers and their biomedical applications.

New Collaboration with a DoD Laboratory

A collaborative, funded program was initiated with researchers at the Naval Weapons Center (Dr. Geoff Lindsay) entitled "Synthesis of Electrochemically Switchable Conducting Polymer Films."

New Personnel

Dr. J. R. Dharia joined our group as a postdoctoral fellow.